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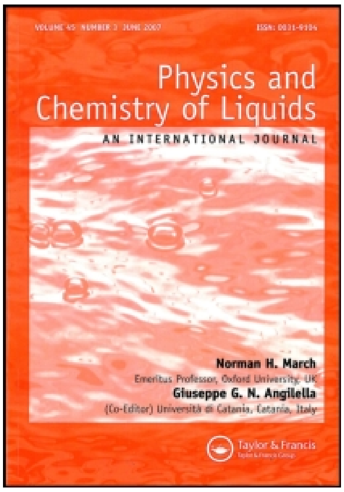

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P. A. Egelstaff[a]

[a] Physics Department, University of Guelph, Guelph, Ontario, Canada

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The Intermolecular Electron Density Distribution in Liquid Nitrogen

P. A. EGELSTAFF

Physics Department, University of Guelph, Guelph, Ontario, Canada N1G 2W1

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The difference between the X-ray diffraction pattern from free nitrogen molecules and that predicted by the independent atom model is deduced from the experimental difference reported for electron diffraction. For liquid nitrogen the most recent and precise X-ray and neutron diffraction data are compared and shown to differ in a different way to the free molecule results. This is interpreted as an intermolecular effect arising from the redistribution of electron density in the chemical bond. It is suggested that as a first approximation the nitrogen molecule should be treated as a linear tricentre in the interpretation of X-ray data.

INTRODUCTION

Nitrogen is a relatively tightly bound molecule and is sometimes regarded as an "ideal" rigid molecule for temperatures below room temperature. The molecular bonding involves about three electrons per atom and consequently it is known that the electron density distribution differs somewhat from that obtained by adding together two free atoms (the independent atom model). This difference has some effect on the diffraction of X-rays and electrons. In the case of electron diffraction the modifications to the scattering by free molecules have been explored experimentally,[1,2] and are well established. In this paper we first try to deduce the X-ray effect for the free molecule from the known electron data. Then we study the magnitude of this effect for liquid nitrogen since it may be observed through differences between the neutron and X-ray diffraction data. It will be pointed out that significant differences can be observed which, in spite of experimental errors, are probably real.

In Section 2, the analysis of diffraction data in this way will be described, in Section 3 we review the data on the free molecule and finally in Section 4 recent X-ray and neutron data on liquid nitrogen are compared. This comparison suggests that the intermolecular electron density distribution must be considered in a sophisticated way if X-ray data is to be interpreted properly, and it will be suggested that as a first approximation the X-ray data should be interpreted as though nitrogen were a linear triatomic molecule.

2 ANALYSIS OF DIFFRACTION DATA

In radiation scattering work we are interested in making measurements of quantities as a function of the scattering vector, $\mathbf{q}$:

$$\mathbf{q} = \mathbf{k}_0 - \mathbf{k} \tag{1}$$

there $\mathbf{k}_0$ and $\mathbf{k}$ are the wave vectors of the incident and scattered radiation respectively. The energy (K) of the radiation is related to $|\mathbf{k}| = k$, by the relativistic equation:

$$K = c(\sqrt{m^2c^2 + \hbar^2k^2} - mc) \tag{2}$$

where m is the rest mass of, for example, the electron, neutron or photon. During the scattering process some energy transfer takes place and this is found from the difference $K_0 - K$. For ideal results the scattering should be nearly elastic that is:

$$K_0 - K \ll K_0 \tag{3}$$

so that $K_0 \simeq K$, or from (2) $k_0 \simeq k$. In this case (1) gives the familiar result:

$$q \simeq 2k_0 \sin \theta/2 \tag{4}$$

where θ is the angle of scatter. We assume either that the experiments have been conducted in the limit (3) or that corrections have been applied to the data to cast them into this limit. Thus we shall consider a normalized differential cross section per atom, subject to Eq. (3), i.e.:

$$\frac{1}{b^2}\frac{d\sigma}{d\Omega} \tag{5}$$

and denote by $E(q)$, $X(q)$ or $N(q)$ this quantity for electrons, X-rays or fast neutrons respectively. The scattering length, b, is for electrons $2/aq^2$ and for X-rays $\lambda\!\!\!^{-}_c{}^2/a$ where a is the Bohr radius and $\lambda\!\!\!^{-}_c$ is the Compton wavelength. For neutrons b is the coherent scattering length for a single nucleus, and we assume that the incoherent neutron scattering has been discarded from the cross section (5). (Note: the Compton scattering of χ-rays is often termed "incoherent" whereas the analogous process for electrons or neutrons is termed "inelastic scattering"; we shall use the latter terminology in this paper.) With these definitions the traditional[2] treatment of electron and X-ray data gives:

$$E(q) \simeq (Z - F(q))^2 N(q) + C(q) \tag{6}$$

$$X(q) \simeq F^2(q) N(q) + C(q) \tag{7}$$

where $C(q)$ is the Compton or inelastic scattering factor, $F(q)$ is the X-ray atomic form factor and Z is the atomic number. Sometimes this approximation is called the independent atom model, and Eqs. (6) and (7) are often employed to reduce the electron or X-ray data to equivalent fast neutron data. By "fast" neutrons we mean neutrons of ~30 eV and for this case there is no equivalent of $C(q)$ as the nuclear level spacing is $\sim 10^6$ eV.

In this paper we are interested in the differences between the approximations (6) and (7) and the observed quantities, namely:

$$\Delta E(q) = E(q) - (Z - F(q))^2 N(q) - C(q) \tag{8}$$

$$\Delta X(q) = X(q) - F^2(q) N(q) - C(q) \tag{9}$$

Egelstaff, March and McGill[3] point out that if the differences $\Delta E(q)$ and $\Delta X(q)$ are significant then one may separate out a nuclear-nuclear, nuclear-electron and an electron-electron correlation function for any system. Using their Eqs. (9), (14), (15) we find

$$\Delta X(q) - \Delta E(q) = S_{ne}(q) - 2ZF(q) S_{nn}(q) = \Delta_{ne} \tag{8'}$$

$$\Delta X(q) = S_{ee}(q) - F^2(q) N(q) - C(q) = \Delta_{ee} \tag{9'}$$

where $S_{nn}(q)$, $S_{ee}(q)$ and $S_{ne}(q)$ are the nuclear-nuclear, electron-electron and nuclear-electron structure factors respectively and Δ_{ee} and Δ_{ne} are the differences between these quantities and their approximate values obtained by use of the approximations defined by Eqs. (6) and (7).

Alternatively we have for single isolated molecules:

$$\Delta_{ne} = Z \int_0^\infty j_0(qr) \Delta D(r) \tag{8''}$$

and

$$\Delta_{ee} = -\frac{1}{2} \int_0^\infty j_0(qr) \Delta P(r) \tag{9''}$$

where $P(r)$ and $D(r)$ are defined by Kohl and Bartell,[4] and are respectively the molecular electron-electron and nuclear-electron correlation functions averaged over angles and molecular vibrations.[5,6] In Eqs. (8″) and (9″), $\Delta P(r)$ and $\Delta D(r)$ are the differences between the true values of these functions and the values obtained from the approximation defined by (6) and (7).

In the case of a dense fluid we may divide $\Delta X(q)$ into intra- and inter-molecular parts. We shall assume that the intra- part is the same as that for the free molecule so that:

$$\Delta X_i(q) \simeq \Delta X_l(q) - \Delta X_f(q) \tag{10}$$

where the subscripts i, l, f mean the inter-molecular, liquid and free molecule terms respectively. In the following sections we try to estimate ΔX_f and ΔX_l, and because we shall show that $\Delta X_l \gg \Delta X_f$ only a rough estimate of ΔX_f will be needed to find ΔX_i. It should be noted that $N(q)$ for the free molecule is known from a standard formula,[7] so that for this case only $X(q)$ and $E(q)$ are unknown.

3 AN ESTIMATE OF $X_f(q)$

We are not aware of X-ray diffraction, data of high quality, on the free molecule. However several electron diffraction measurements[1,8] have been made which give $\Delta E(q)$ in Figure 1, and so we shall attempt to obtain an

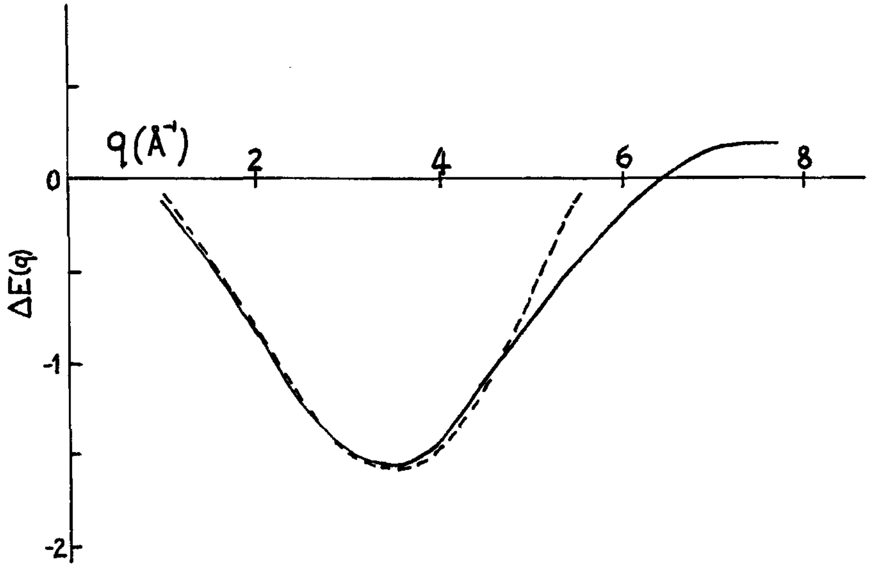

FIGURE 1 The experimental function $\Delta E(q)$—full line—from Ref. 8, and the prediction of the primitive model (Section 3, Eq. (12))—dashed line.

approximation to $\Delta X(q)$ by relating it to $\Delta E(q)$ using approximate methods and models.

For low values of q the elastic scattering is dominant, and therefore for the first model it will be assumed that differences from the independent atom model (of Eqs. (6) and (7)) occur solely in the elastic scattering. In this model $C(q)$ is the same as for the free atom. Then it will be assumed that the molecular electron density may be divided into $(7 - \delta)$ electrons/atom which are centred on the nuclei with a form factor $F(q)$, and δ electrons-atom which are distributed in pieces δ_i among sites on the internuclear axis in real space, x_i, with form factors $f_i(q)$ in Fourier space. For this model the expressions for $E(q)$ and $X(q)$ may be written down and expanded to first order in the δ_i. This allows the following ratio to be calculated from Eqs. (8) and (9):

$$\frac{\Delta X(q)}{\Delta E(q)} = -\frac{F(q)}{7 - F(q)} + 0(\delta) \qquad (11)$$

This is the required equation and the predicted $\Delta X(q)$ is shown in Figure 2; however it would be useful to test the applicability of this model by comparing predicted and measured results for $\Delta E(q)$. To do this a primitive version of the model will be used in which there is only one auxiliary site at the centre of the bond $(x_i = 0)$ containing δ electrons/atom and the form factor $f_i(q)$ is assumed to be constant for $q < 5A^{-1}$, (i.e. to vary much more slowly with q than $F(q)$ so that the δ electrons are significantly more localised than those in an N atom). In this case:

$$\Delta E(q) \simeq -4\delta(7 - F(q))\left\{j_0\left(\frac{dq}{2}\right) - \frac{N(q)F(q)}{14}\right\} + 0(\delta^2) \qquad (12)$$

The only adjustable parameter is δ and by taking $\delta = 0.35$ electrons/atom the dashed curve in Figure 1 is found for $q < 5A^{-1}$. At high q the behaviour

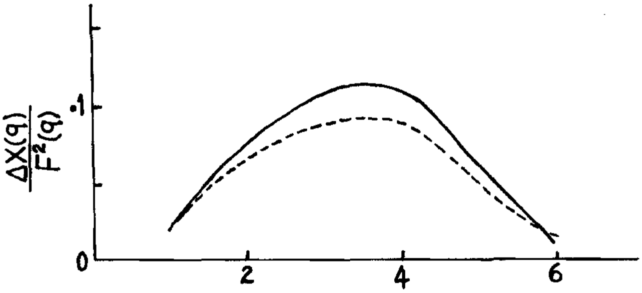

FIGURE 2 The function $\Delta X(q)/F^2(q)$ for model 1—full line, and model 2—dashed line. The data are divided by $F^2(q)$ in order that the scale is the same as that usually employed for X-ray results.

of $f(q)$, the terms of $0(\delta^2)$ and the inelastic scattering become important and therefore a fit of this quality may be fortuitous. Nevertheless to require ~5% of the electron density to be displaced is reasonable[9] (e.g. ~8% is required at the centre to obtain the experimental quadrupole moment) and so this model is plausible. We note that in this "primitive model" the nitrogen molecule looks like a linear tricentre as far as the electrons are concerned.

A second model may be obtained by modifying the independent atom model. For this case we assume that the most important modification to the electronic distribution arises from small changes $\varepsilon_j(q)$ in the atomic form factors $f_i(q)$ for the unperturbed electronic states j only. To complete this model we assume $\varepsilon_j(q)$ is independent of j for Z' valence electrons and is zero for the remaining electrons. After expanding to first order in ε_j we find that $F(q)$ and $C(q)$ in (6) and (7) should be modified by adding:

$$\Delta F(q) \simeq Z'\varepsilon(q) \text{ and } \Delta C(q) \simeq -2\varepsilon(q)\frac{Z'}{Z}F(q) \qquad (13)$$

Using this model for $E(q)$ and $X(q)$ in Eqs. (8) and (9) and then eliminating $\varepsilon(q)$ we obtain finally:

$$\Delta X_f(q) \simeq -\Delta E_f(q)\left\{\frac{Z^2N(q)}{F(q)(ZN(q)-1)} - 1\right\} \qquad (14)$$

The predictions of this formula are shown in Figure 2 also, and are in reasonable agreement with the first model. Since this model makes a different approximation to the elastic scattering and partially corrects the inelastic scattering, the agreement with the first model is encouraging.

It is concluded that $\Delta X_f(q)$ is known approximately and in what follows the mean of the two curves in Figure 2 will be used. Nevertheless it would be worthwhile to have some direct experimental measurements of $\Delta X_f(q)$.

4 STRUCTURE FACTORS FOR LIQUID NITROGEN

In the case of liquid nitrogen there are several X-ray and neutron structure factor measurements which are stated to be accurate to about 1% so that small changes in $X(q)$ of the size shown in Figure 2 might be observed. The most recent and precise data will be used here, but even so we have found it necessary to critically re-evaluate these data.

We have found it necessary to reanalyse the neutron data of Clarke *et al.*[10] They used four wavelengths (0.35; 0.70; 0.84 and 1.06 Å), but $\lambda = 0.35$ and 0.84 Å are of lower quality than the other wavelengths and will not be used here. Then the $d\sigma/d\Omega$ data must be corrected to satisfy Eq. (3)—excluding a term due to molecular vibrations. Clarke *et al.*[10] used a formula which

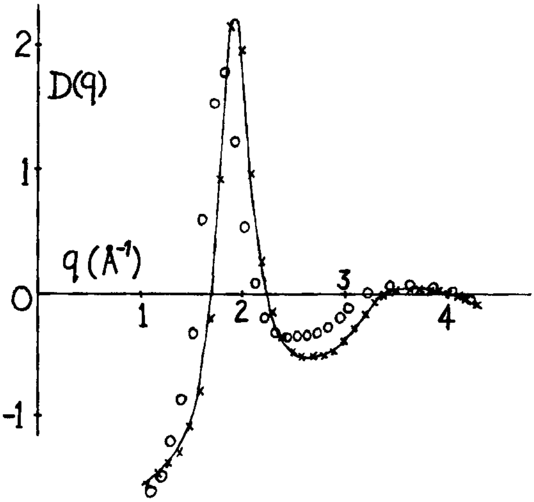

FIGURE 3 The significant section of the neutron data of Ref. 10 (λ = 0.7 Å) presented as $D_n(q)$, Eq. (15)—circles, and the X-ray data of Ref. 13, presented as $D_x(q)$, Eq. (16)—crosses. A line is drawn through the X-ray data as a guide for the eye. The neutron data for λ = 1.06 Å are in agreement with λ = 0.7 Å and are not shown here.

corrects for the recoil effect but does not include the thermal motion of the molecules, and also they employed empirical constants in it (rather than, e.g., using the actual mass of nitrogen atoms). We have employed the formulae of Egelstaff and Soper[11] which include both the effects of nuclear recoil and thermal motion (which is small in this case) and contain only the known properties of the nitrogen molecule. In this way we have converted the table of differential cross sections in Clarke *et al.*'s paper to $N(q)$. We stress that neither a scale factor nor an adjustable constant has been used in our data reduction. We express the result as:

$$D_n(q) = N_l(q) - N_f(q) \tag{15}$$

and these data are shown in Figure 3. Clarke *et al.*'s data were taken for T = 77 K and a pressure of 1 atmosphere (the normal boiling point). For X-rays Furumoto and Shaw[12] worked at 65 and 77 K, while X-ray data of higher quality were taken by Narten *et al.*[13] for a temperature of 65 K. In the later work the free atom form factor was used and the Compton subtraction was done partly experimentally, through their graphite monochromator, and partly empirically by adjusting the monochromator resolution function so that the Fourier transform of $D_x(q)$ (Eq, (16)) showed no structure at low r. Unfortunately this means that the part of the transform of $\Delta X(q)$ at $r < 3$ Å has been removed artificially from the data. Nevertheless the data of

Narten *et al.* are the best available at the moment, and are plotted in Figure 3 as the function:

$$D_x(q) = \frac{X_l(q) - X_f(q)}{F^2(q)} \tag{16}$$

The table in Narten *et al.*'s[13] paper is based on the assumption that Eq. (7) is a good approximation for $X_f(q)$, and therefore we have revised their data in the light of the free molecule discussion of Section 3.

It can be seen that there are significant shifts in q scale and in magnitude between the neutron and X-ray data of Figure 3. In the next section we discuss these differences in relation to the changes expected because of the difference in temperatures used. It will be shown that the change in amplitude is expected but that the positional changes are not. Nevertheless it would be desirable to have good experimental X-ray and neutron data for the same state.

5 COMPARISON OF STRUCTURE FACTORS AND CORRELATION FUNCTION AT 65 AND 77 K

Between these two states the density changes by 6.7% and the temperature by 18.5% so that some readily observable changes in the structure factors may be expected.

Since Furumoto and Shaw[12] have X-ray data (of limited quality) at both 65 and 77 K it is worth using their results to study these shifts. Their data are shown in Figure 4 and it can be seen that to a first approximation there

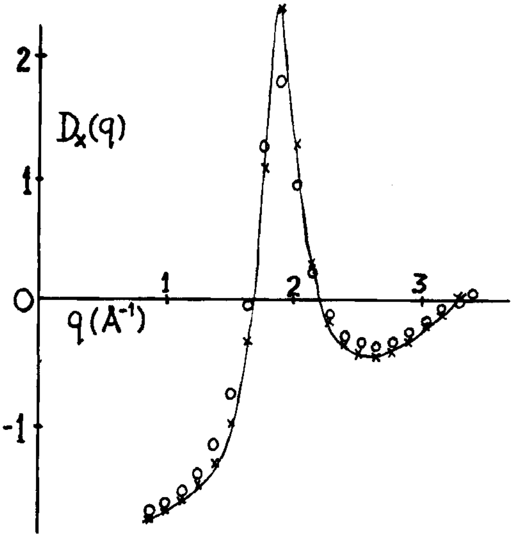

FIGURE 4 The X-ray data of Ref. 12 for liquid nitrogen at 65 K—crosses, and 77 K—circles.

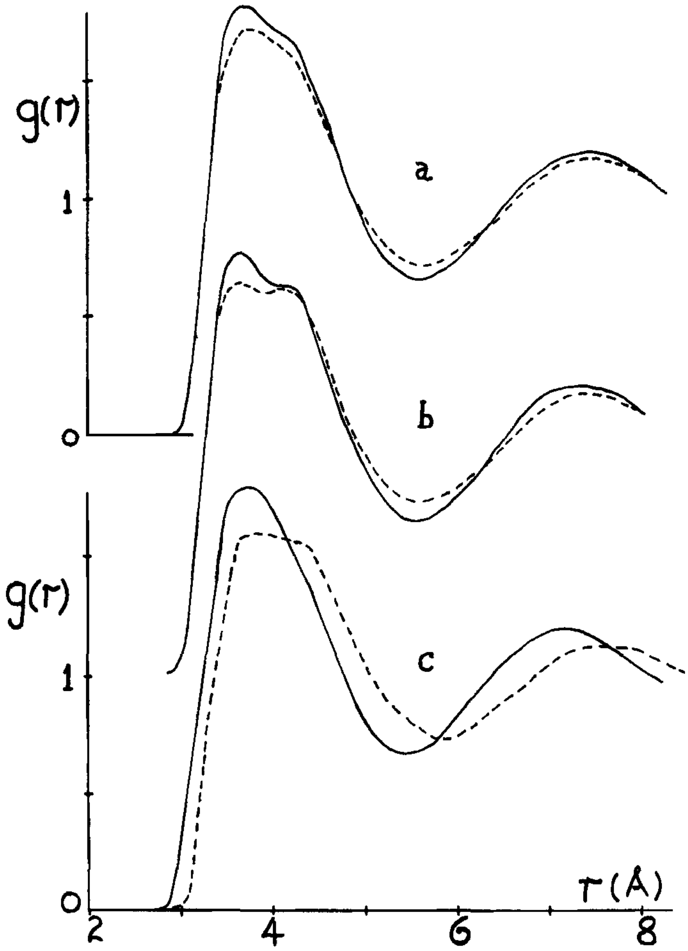

FIGURE 5 (a) Computer simulation of $g(r)$ for liquid nitrogen at 65 K—full line and 77 K—dashed line, using a site-site interaction potential.[15] (b) As (a) but for site-site plus quadrupole interaction. (c) The Fourier transforms of the data of Refs. 10 and 13; X-ray data at 65 K—full line, neutron data at 77 K—dashed line.

is an amplitude change of about 10%, and the shift in q cannot be determined (<0.03 Å^{-1}). This is in contrast to the shift in Figure 3 of $\simeq 0.1$ Å^{-1}.

Such state changes may be studied also by computer simulations. In Figure 5 we show the data of Haile[14] who used the site-site and site-site plus quadruples models of Cheung and Powles.[15] Also shown in this figure is the Fourier transformation to r-space of the data of Refs. 10 and 13. Again it is seen that the simulations show an amplitude change of ~8% together with only a small shift of ~0.02 Å in r, whereas the X-ray and neutron data show a shift of ~0.2 Å.

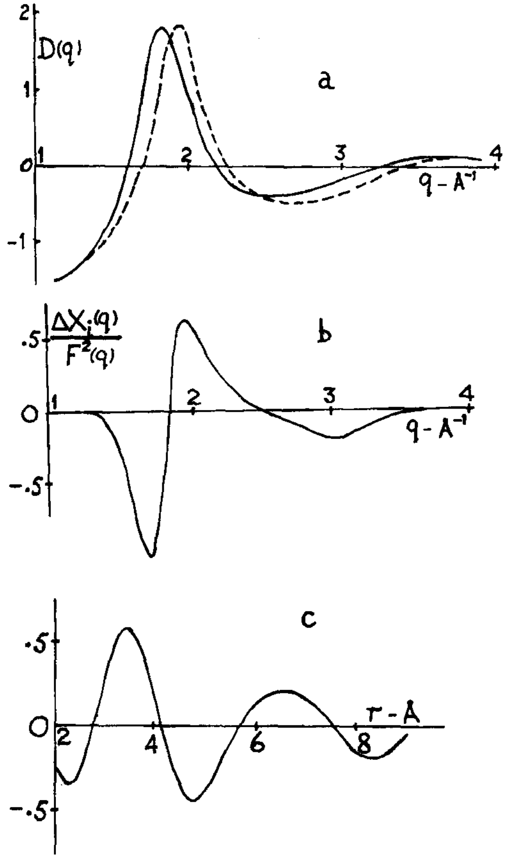

FIGURE 6 (a) The interference functions $D_n(q)$ and $D_x(q)$ for liquid nitrogen at 77 K and 1 atm. (b) The function $\Delta X_i(q)$ computed from the results shown in 6a. (c) The Fourier transform of the data of Figure 6b.

It is possible that some of the latter difference is due to experimental error. However the error in the q scale is of the same order as the error in the wavelength and in the measurement of the angle θ. The combined (λ, θ) error in a modern instrument is less than 0.5% whereas the shift shown in Figures 3 and 5 is ~5%.

We conclude, therefore, that the principal effect due to the state change is a reduction in amplitude of $D(q)$ by ~10%. A change to the data of Narten *et al.* will be made before calculating $\Delta X_1(q)$. This is done by drawing a smooth curve through the ratios of Furumoto and Shaws[12] data at 77 and 65 K and applying the smoothed ratios to the data of Narten *et al.* The modified X-ray and the neutron data are shown in Figure 6a.

6 AN ESTIMATE OF $X_i(q)$ AND DISCUSSION

After applying the modification discussed above to the X-ray data, the quantity $\Delta X_i(q)$ has been evaluated from Eq. (10). It is shown in Figure 6b together with its Fourier transform in 6c. In contrast to $\Delta X_f(q)$ in Figure 2, the principal intensity is found for lower q and the shape is different. This suggests that $\Delta X_i(q)$ is a significant quantity which needs to be analysed in order to interpret X-ray data.

The r-space results of Figures 5c and 6c suggests that the electron density of two molecules can be found at shorter (mean) separations than can the nuclear density. If the primitive model of electron redistribution (Section 3) is combined with the expected distribution of molecular orientations,[16] it can be seen that the electron density in the molecular centre will lead to some shorter separations. [In Figure 6c we do not show the structure below 3 Å because (Section 4) the X-ray data has not been corrected properly for Compton Scattering and this has left some artificial structure in the region $r < 3$ Å.]

A crude explanation of the data in Figure 6c may be obtained again by using the primitive model of Section 4. In this model the X-ray results should be interpreted as though the molecule were a linear triatomic (B–A–B) and the neutron results interpreted as for a linear diatomic (B–B). Since A is a weak scatterer with a small diameter, the transform of $\Delta X_i(q)/F^2$ is similar to the cross correlation function $g_{AB}(r) - 1$ for a linear triatomic in which the diameter of A is less than that of B. The function in Figure 6c has approximately the right shape and peaks in the right position for this model, but the amplitudes are 2–4 times too large. Consequently the original data (Refs. 10 and 13) may include some unspecified experimental errors which are larger than the anticipated ones. Nevertheless we believe that the techniques reported by these authors are capable of measuring the correct size of this effect, and that it is most likely that much of the differences observed are real. Compared to the independent atom model the primitive model can explain the electron diffraction data on the free molecule and can explain qualitatively the X-ray diffraction data on liquid nitrogen. It is therefore an improvement over the former model.

We conclude that the redistribution of electron density in the chemical bond leads to significant differences in the intermolecular structure for electrons compared to nuclei. However further experiments would be desirable on both the free molecule and the liquid to test the existing data for unforseen experimental errors and to enlarge on the present conclusions.

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5. The relationship between our quantities and those used in Ref. 4 is $\Delta_{ee} = \Delta\sigma_{ee}/2$; $\Delta_{ne} = -\Delta\sigma_{ne}/2$.
6. Our normalisation implies that the usual structure factor obtained in X-ray or neutron diffraction experiments tends to unity at high q.
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